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71 Applicant: **MOBIL OIL CORPORATION**
150 East 42nd Street
New York New York 10017(US)

72 Inventor: **Abramo, Guy Paul**
215 Loring Court
Sewell New Jersey 08080(US)
Inventor: **Trewella, Jeffrey Charles**
8 Morgan Road
Flemington New Jersey 08822(US)

74 Representative: **Colmer, Stephen Gary**
Patent Department c/o Mobil Services
Company Limited Mobil Court 3 Clements
Inn
London WC2A 2EB(GB)

54 **Mannich base deposit control additives and fuel compositions containing same.**

57 Disclosed is an additive for fuel compositions comprising a mixture of (1) a hydroxyalkylaryl amine (phenolic Mannich base), and (2) a polyalkylene. Also disclosed is the resulting fuel composition made up of a major amount of diesel or gasoline fuel and a minor amount of the aforesaid mixture and a method for reducing deposits in gasoline internal combustion engines using such compositions.

EP 0 376 563 A1

MANNICH BASE DEPOSIT CONTROL ADDITIVES AND FUEL COMPOSITIONS CONTAINING SAME

This invention relates to additives for controlling or preventing engine deposits, to fuel compositions containing these additives and to methods for reducing deposits in gasoline internal combustion engines using such additives.

Mannich bases are disclosed in U.S. Patent No. 4,116,644 as a component of a concentrate along with a demulsifying agent, a mono-or dinuclear aromatic hydrocarbon solvent, an alkanol, and a corrosion inhibitor. U.S. Patent No. 4,259,086 discloses substituted phenol/epichlorohydrin/amine adducts as additives for hydrocarbon fuels. U.S. Patent No. 4,787,996 discloses Mannich bases prepared using phenol substituted with medium length branched alkyl chains as friction reducing agents in lubricants and fuel compositions.

The present invention provides an additive composition for hydrocarbon fuels consisting essentially of

(a) a polyalkylene, and

(b) a condensation product obtained by reacting an amine with an aldehyde and a phenol.

The present invention also provides a fuel composition comprising a major amount of a liquid fuel and a minor amount of an additive mixture consisting essentially of

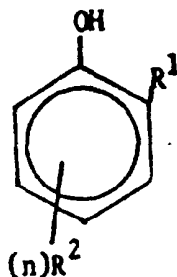
(a) a polyalkylene, and

(b) a condensation product obtained by reacting an amine with an aldehyde and a phenol.

The present invention further provides a method for reducing deposits in gasoline internal combustion engines comprising running the engine with a fuel containing an effective amount, greater than about 45.35 kg per 119.24 kl (100 pounds per thousand barrels) of an additive composition for reducing carbon deposits in internal combustion engines comprising:

(a) a polyalkylene, and

(b) a condensation product obtained by reacting an amine with an aldehyde and a phenol. Mannich base reaction products are well known in the prior art U.S. Patents Nos. 4,116,644 and 4,787,996 discuss the preparation of Mannich bases. Mannich base reaction products are made by reacting an aldehyde, an amine and one or more phenols of the formula:



The phenol can be phenol itself, cresol, xylene, hydroxydiphenyl, amylphenol, benzylphenol, alpha and beta naphthols, decene dimer phenol, decene trimer phenol, decene tetramer phenol, octene dimer and trimer phenol, dodecene dimer and trimer phenol or the dialkyl analogues of these. Of the available phenols the most preferred are the substituted phenols wherein R^2 is not hydrogen.

The phenols used in this invention can be purchased from commercial sources. In general, if desired or necessary, they are readily prepared by adaptation of methods well known in the art. For example, they may be prepared by the acid catalyzed alkylation of phenol with an olefin. In this method a small amount of an acid catalyst such as sulfuric or phosphoric acid, or preferably Lewis acid such as BF_3 -etherate, BF_3 -phenate complex or $AlCl_3 \cdot HSO_4$ is added to the phenol and the olefin then added to the phenol. Additional details of the reaction are found in U.S. Patent 4,116,644.

In the above structural formula R^1 is hydrogen or a C_1 to C_{80} hydrocarbyl group, which may be an alkyl, alkenyl, aryl, alkaryl or aralkyl group. If R^1 is an aryl group it can be one having from 6 to 14 carbon atoms, i.e. phenyl, naphthyl, anthryl or phenanthryl. Preferably, R^1 is hydrogen.

R^2 is hydrogen, hydrocarbyl group, alkyl or alkenyl containing 4 to 80 carbon atoms, and can additionally contain sulfur, oxygen and/or nitrogen atoms. "n" is 0, 1, or 2. Preferably, R^2 is a polymeric group having a molecular weight up to between 1000 and 2000 and can be polypropyl, polybutenyl, polyisobutyl or polydodecyl and preferably is polydecyl.

In carrying out the reaction to form the Mannich base, the phenol:aldehyde:amine molar ratios used can be 1:0.1-10:0.1-10 or broader, respectively.

Aldehydes that can be used are the aliphatic aldehydes, such as formaldehyde or paraformaldehyde, acetaldehyde, and aldol(3-hydroxy butyraldehyde); aromatic aldehydes, such as benzaldehyde and heterocyclic aldehydes, such as furfural. The aldehyde may contain a substituent group such as hydroxyl, halogen or nitro. In short, any substituent can be used which does not take a major part in the reaction. However, preference is given to the aliphatic-aldehydes, formaldehyde being particularly preferred.

The amines to be used include those which contain a primary amino group. Polyalkylene polyamines can be used such as ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, corresponding polypropylene polyamines and similar amines. Of the polyethylene polyamines the most preferred is triethylenetetramine.

Saturated and unsaturated aliphatic amines containing 1 to 20 carbon atoms can also be used. More specifically, they include those of the structural formula:

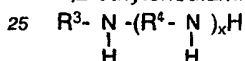


wherein R^3 is a hydrocarbyl group having from 2 to 80 carbon atoms. These are C_6 to C_{18} straight or branched alkyl groups including cocoamine, oleylamine, octylamine, nonylamine, decylamine, dodecylamine, tetradecylamine, hexadecylamine, octadecylamine, cyclooctylamine, laurylamine, isostearylamine, and soyamine but may be cyclic, the latter of which include cyclohexylamine.

Other amines which can be used include:

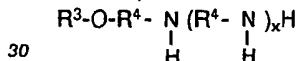
(a) etheramines (hydrocarbyloxy hydrocarbyl amines) such as tri isodecyloxypropyl amine and etheramines of the formula $R^3OR^4NH_2$ where R^3 is as stated above and R^4 is a C_1 to C_6 hydrocarbyl group;

(b) N-hydrocarbyl hydrocarbylene diamines or triamines such as N-oleyl-1,3 propylene or N-coco-1,2-ethylenediamine or amines of the structure



where R^3 and R^4 are as indicated above and x is 1 to 3;

(c) etherdiamines (hydrocarbyloxy hydrocarbyl hydrocarbyl diamines) such as those of the structure



where R^3 and R^4 are as indicated above and x is 1 to 3;

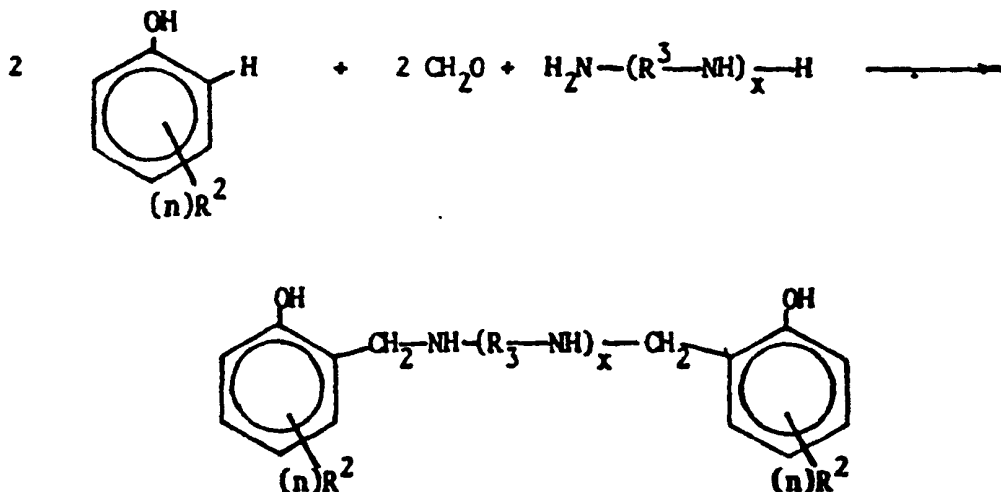
Also useful are aryl-hydrocarbylene amines and diamines.

The reaction between phenol, amine and aldehyde is carried out at from $80^\circ C$ to $150^\circ C$. The temperature chosen will depend for the most part on the particular reactants and on whether or not a solvent is used. While atmospheric pressure is generally preferred, the reaction can be advantageously run at from 1 to 0.5 atmospheres. Furthermore, where conditions warrant it, a solvent may be used. In general, any relatively non-polar, unreactive solvent can be used, including benzene, toluene, xylene and 1,4-dioxane. Other hydrocarbon and alcoholic solvents, the latter which include propanol and butanol can be used. Further, mixtures of hydrocarbons and, for example, alcohols may be advantageous.

While the preferred mode of synthesis of the Mannich base involves a one-step reaction in which all reactants are placed together, other modes can be used. For example, the phenol and amine components can be reacted to yield an ammonium phenate, and this product then reacted with an aldehyde. This mode is not favorable since one tends to get methylene bridged polymers. A third possible scheme involves the reaction of amine and aldehyde to yield a Schiff base ($RN=CH_2$), followed by reaction of the Schiff base with phenol to give the product. Results using this reaction are more favorable than the second scheme mentioned, and they appear to be similar to those from the first reaction.

Reaction times are not critical, and can range from about 1 hour or less up to 8 hours or more, depending, among other things, upon the particular reactants and the solvent used.

The resulting Mannich base component of the mixture of this invention is believed to have the structure shown in the following reaction equation, where R^2 and R^3 are each hydrogen or a hydrocarbyl group of 2 to 80 carbon atoms, n is 0, 1 or 2, and x is 1 to 3; for example, R^2 is a $(C_{10})_3-4$ residue, R^3 is C_2 , "n" averages 1.5 and x is 3.



The polyalkylene component of the additive composition preferably is a liquid polyalkylene where the average number of carbon atoms per molecule is between 12 and 500. Preferably, the polyalkylene is a polymer of ethylene or propylene and, more preferably, is polyisobutylene wherein the average number of carbon atoms per molecule is between 12 and 500.

The additive composition is formulated by mixing the components in the following proportions:

	Parts by Weight
Mannich base	30 to 46
Polyalkylene	50 to 74

In general, the invention contemplates the use of the additive mixture in a fuel composition in a concentration of from 45.36 kg to 81.65 kg per 119.24 kl (100 lbs. to 180 lbs. per 1,000 barrels) of fuel, and most preferably, from 54.43 kg to 72.57 kg per 119.24 kl (120 lbs. to 160 lbs. per 1,000 barrels). If gasoline is the base fuel, it contains preferably less than 0.1 weight percent sulfur. Since sulfur and olefins are believed to contribute to gum formation, their reduction is advantageous in obtaining good cleanliness performance. The gasoline can also contain conventional additives such as antioxidants, metal deactivators, lead alkyls, lead scavengers and corrosion inhibitors.

EXAMPLE 1

Premium unleaded gasoline containing various quantities of a hydroxyalkarylamine (Mannich base) and polyalkylene mixed in the ratios shown below were evaluated in a single cylinder CLR engine using a 10W-30 mineral oil. After 40 hours of operation at 1100 rpm and 10 to 12 inches manifold vacuum, the intake valve (ITV) was removed, its combustion chamber side cleaned and the gross weight determined. Deposits were then removed mechanically and the valve's tare weight was measured in order to calculate the net weight of the deposits.

The table below presents the results for several runs with premium unleaded gasoline containing various additive package components alone and in combinations. As indicated, use of the Mannich base alone at 24.95 kg per 119.24 kl (55 pounds per 1000 barrels, Run B) increased ITV deposits 231% compared to Run A in which no additive was present in the fuel. Using a higher dosage of this material 79.38 kg per 119.24 kl (175 pounds per 1000 barrels, Run C) also increased ITV deposits significantly. Polyalkylene alone at 45.36 kg per 119.24 kl (100 pounds per thousand barrels, Run D) did reduce ITV deposits to 37% of Run A. However, a significant further reduction in deposits was obtained when a package of the type described herein was used in Run E. Use of mixtures outside this invention as in Run F

did not provide any substantially improved performance.

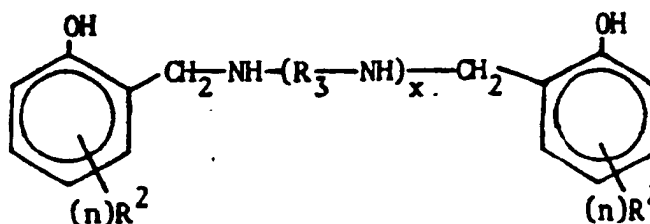
Table II

	CLR intake Valve Cleanliness Test Results			
	Concentration of Fuel Kilograms per 119.24 Kiloliters (Pounds per 1000 Barrels of Fuel)		Intake Valve Deposits Weight, Milligrams	Percent Deposits vs Base
	Mannich Base	Polyalkylene		
A	-	-	298*	
B	25 (55)	-	688	231
C	79.5 (175)	-	439	147
D	-	45.5 (100)	109	37
E	25 (55)	40.9 (90)	47	16
F	4.2 (10.5)	43.0 (94.5)	196	66

*Average of 8 runs

Claims

1. An additive composition for hydrocarbon fuels consisting essentially of
 - (a) a polyalkylene, and
 - (b) a condensation product obtained by reacting an amine with an aldehyde and a phenol.
2. The additive composition of claim 1 wherein the condensation product is a phenol amine aldehyde condensation product of the structural formula



wherein R^2 and R^3 are each hydrogen or hydrocarbyl group of 2 to 80 carbon atoms, n is 0, 1, or 2 and x is 1 to 3.

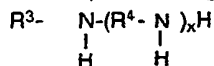
3. The additive composition of claim 1 wherein the condensation product is the condensation product of
 - (a) a phenol selected from cresol, xlenol, hydroxydiphenyl, amylphenol, benzylphenol, alpha and beta naphthols, decene dimer phenol, decene trimer phenol, decene tetramer phenol, octene dimer and trimer phenol, dodecene dimer and trimer phenol or the dialkyl analogues of these;
 - (b) an aldehyde selected formaldehyde, paraformaldehyde, acetaldehyde, aldol(3-hydroxy butyraldehyde), benzaldehyde and furfural; and
 - (c) an amine selected from cocoamine, oleylamine, octylamine, nonylamine, decylamine, dodecylamine, tetradecylamine, hexadecylamine, octadecylamine, cyclooctylamine, laurylamine, isostearylamine, soyamine, cyclohexylamine, ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, corresponding propylenepolyamines, triisodecyloxypropyl amine and N-oleyl-1,3 propylene or N-coco-1,2-ethylenediamine
4. The additive composition of claim 1 wherein the condensation product is the condensation product of:
 - (a) a phenol selected from decene trimer phenol and decene tetramer phenol;
 - (b) formaldehyde;

(c) triethylenetetramine.

5. The additive composition of claim 1 wherein the amine has the formula R^3NH_2

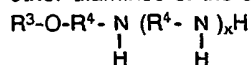
where R^3 is a hydrocarbyl group having 2 to 80 carbon atoms.

6. The additive composition of claim 1 wherein amine is selected from etheramines having the structural formula, $R^3OR^4NH_2$, hydrocarbyl hydrocarbylene polyamines of the structural formula



and

ether diamines of the structural formula



where R^3 is a hydrocarbyl group having from 2 to 80 carbon atoms, R^4 is a hydrocarbyl group of 1 to 6 carbon atoms, and x is 1 to 3.

7. The additive composition of claim 1 wherein the amine, aldehyde, and phenol are reacted in a molar ratio of phenol:aldehyde:amine of 1:01 to 10:01 to 10, respectively.

8. The additive composition of claim 1 wherein the polyalkylene is a liquid polyalkylene in which the average number of carbon atoms per molecule is between 12 and 500.

9. The additive composition of claim 1 wherein said polyalkylene is polybutylene in which the average number of carbon atoms per molecule is between 12 and 500.

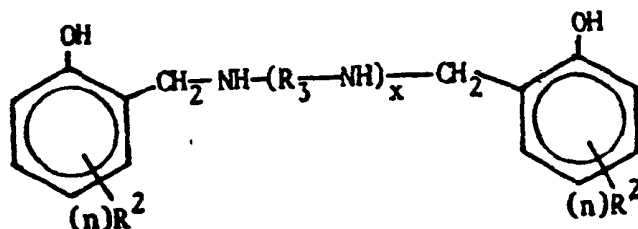
10. The additive composition of claim 1 wherein the additive contains between 50 and 74 parts by weight of polyalkylene and between 30 and 46 parts by weight of condensation product.

11. A fuel composition comprising a major amount of a liquid fuel and a minor amount of additive mixture consisting essentially of

(a) a polyalkylene, and

(b) a condensation product obtained by reacting an amine with an aldehyde and a phenol.

12. The fuel composition of claim 11 wherein the condensation product is a phenol amine_aldehyde condensation product of the structural formula



wherein R^2 and R^3 are each hydrogen or hydrocarbyl group of 2 to 80 carbon atoms, n is 0, 1 or 2 and x is 1 to 0.

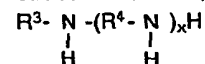
13. The fuel composition of claim 11 wherein the condensation product is the condensation product of a polydecyl phenol, formaldehyde, and triethylenetetramine.

14. The fuel composition of claim 11 wherein the amine has the formula



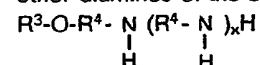
where R^3 is a hydrocarbyl group having 2 to 80 carbon atoms.

15. The fuel composition of claim 11 wherein the amine is selected from etheramines having the structural formula, $R^3OR^4NH_2$, hydrocarbyl hydrocarbylene diamines of the structural formula



and

ether diamines of the structural formula



where R^3 is a hydrocarbyl group having from 2 to 80 carbon atoms, R^4 is a hydrocarbyl group of 1 to 6 carbon atoms, and x is 1 to 3.

16. The fuel composition of claim 11 wherein the polyalkylene, is selected from polyethylene, polypropylene, and polyisobutylene.

17. The fuel composition of any one of claims 11 to 16 wherein the amine, aldehyde, and phenol are

reacted in a molar ratio of phenol:aldehyde:amine of 1:0.1 to 10:0.1 to 10, r respectively.

18. The fuel composition of claim 11 wherein the polyalkylene is a liquid polyalkylene in which the average number of carbon atoms per molecule is between 12 and 500.

19. The fuel composition of claim 18 wherein the polyalkylene is polyisobutylene in which the average number of carbon atoms per molecule is between 12 and 500.

20. The fuel composition of any one of claims 11 to 19 wherein the additive contains between 50 and 74 parts by weight of polyalkylene and between 30 and 46 parts by weight of condensation product.

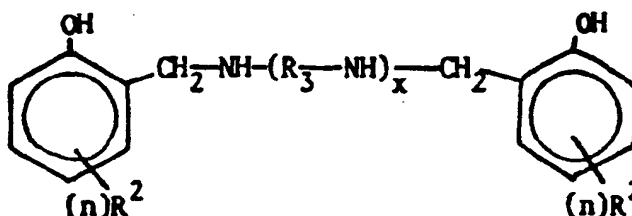
21. The fuel composition of any one of claims 11 to 20 wherein the additive mixture is present in the fuel composition in an amount of between 45.35 kg and 81.65 kg per 119.24 kl (100 and 180 pounds per 1000 barrels) of fuel.

22. A method for reducing deposits in gasoline internal combustion engines comprising running the engine with a fuel containing an effective amount, greater than about 45.35 kg per 119.24 kl (100 pounds per thousand barrels) of an additive composition for reducing carbon deposits in internal combustion engines comprising:

(a) a polyalkylene, and

(b) a condensation product obtained by reacting an amine with an aldehyde and a phenol.

23. The method of claim 22 wherein the condensation product is a phenol amine aldehyde condensation product of the structural formula



wherein R^2 and R^3 are each hydrogen or hydrocarbyl group of 2 to 80 carbon atoms, n is 0, 1 or 2 and x is 1 to 3.

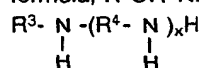
24. The method of claim 22 wherein the condensation product is the condensation product of polydecyl phenol, formaldehyde, and triethylenetetramine.

25. The method of claim 22 wherein the amine has the formula



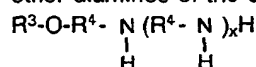
where R^3 is a hydrocarbyl group having 2 to 80 carbon atoms.

26. The method of claim 22 wherein the amine is selected from etheramines having the structural formula, $R^3OR^4NH_2$, hydrocarbyl hydrocarbylene diamines of the structural formula



and

ether diamines of the structural formula



where R^3 is a hydrocarbyl group having from 2 to 80 carbon atoms, R^4 is a hydrocarbyl group of 1 to 6 carbon atoms, and x is 1 to 3.

27. The method of claim 22 wherein the polyalkylene, is selected from polyethylene, polypropylene and polyisobutylene.

28. The method of any one of claims 22 to 27 wherein the amine, aldehyde, and phenol are reacted in a molar ratio of phenol:aldehyde:amine of 1:0.1 to 10:0.1 to 10, respectively.

29. The method of claim 22 wherein the polyalkylene is a liquid polyalkylene in which the average number of carbon atoms per molecule is between 12 and 500.

30. The method of claim 22 wherein polyalkylene is polybutylene in which the average number of carbon atoms per molecule is between about 12 and about 500.

31. The method of claim 22 wherein the additive contains between about 50 and about 74 parts by weight of polyalkylene and between about 30 and about 46 parts by weight of condensation product.

32. The method of any one of claims 22 to 31 wherein the additive mixture is present in the fuel composition in an amount of between 54.43 kg and 72.57 kg per 119.24 kl (120 and 160 pounds per 1000 barrels) of fuel.



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EUROPEAN SEARCH REPORT

Application Number

EP 89 31 3173

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-3 948 619 (WORREL) * Whole document; column 11, lines 23-29 *	1,5,6,8 -11,14- 16,18- 20,22, 25-27, 29-31	C 10 L 1/14
Y	---	2,3,4,7 ,12,13, 17,21, 23,24, 28,32	
Y	US-A-3 649 229 (OTTO) * Examples 3,4,6; claims 1,2,5-10 *	2,7,12, 17,21, 23,28, 32	
Y	---		
Y	EP-A-0 182 940 (MOBIL OIL CORP.) * Claim; pages 11-14 *	3,4,13, 24	
A	---		
A	US-A-4 032 304 (DORER Jr. et al.) * Abstract; column 4, line 64 - column 5, line 2; column 7, line 32 - column 8, line 64 *	1,6,11, 15,22, 26	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	---		C 10 L
A	GB-A- 773 489 (CHEMISCHE WERKE HULS AKT.) * Whole document *	6,15,26	
A	---		
A	US-A-4 054 422 (GARTH) * Whole document *	1,2,11, 12,22, 23	
A	---		
A	US-A-3 647 404 (SWEENEY et al.) * Whole document *	1-32	

	-/-		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 07-03-1990	Examiner DE LA MORINERIE B.M.S.B.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	GB-A-2 010 324 (CHEVRON) * Whole document * -----	1-32	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 07-03-1990	Examiner DE LA MORINERIE B.M.S.B.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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